

Annual Progress Report:
Surface Chemistry and Tribology of
Carbide and Nitride Hard Coatings

20 January 2000

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Prepared for

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Engineering and Technology Group

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**ANNUAL PROGRESS REPORT:
SURFACE CHEMISTRY AND TRIBOLOGY OF
CARBIDE AND NITRIDE HARD COATINGS**

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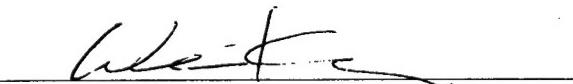


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Abstract

This report summarizes The Aerospace Corporation's efforts in the third year of our AFOSR-funded joint research program with the University of Houston (UH). We completed surface science studies on the interaction of carbon monoxide, ammonia, and a series of small alcohols with the TiC and VC (100) surfaces using high-resolution electron energy-loss spectroscopy (HREELS) and X-ray photoelectron spectroscopy (XPS). We hosted visits by UH personnel, and visited UH twice to perform experiments and discuss results. Our results were presented at two national scientific conferences, and two documents were submitted for publication. Finally, we formulated plans with UH and wrote a proposal for a follow-on three-year program extending this work. Our work is on schedule as outlined in our proposal. The following report is in the format specified by the funding agency for inclusion in the full program report prepared by UH.

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Objectives

The objectives are unchanged from the original proposal.

Status of Effort

Our effort is on schedule as outlined in the proposal. During the reporting period, we advanced our study of titanium carbide (TiC) and vanadium carbide (VC) (100) surface chemistry to investigate reactions with adsorbates of increasing complexity and technical relevance. Adsorbates have included water, considered important from an environmental perspective, carbon monoxide and ammonia, as probes of the electronic structure model developed within this program, and a series of alcohols, including methanol, ethanol, and trifluoroethanol, as probes of interfacial reactivity with lubricant analogs. In addition to demonstrating unique reactivities for the different classes of adsorbates, these studies also continue to reveal substrate-dependent reactivities. Our Aerospace Independent Research and Development (IR&D) program has provided significant funding to augment our work in this program, and we have used funds from this AFOSR grant to foster our collaborative effort. Our primary use of this grant is to provide UH with results and insight from work generated in our IR&D effort once they have been cleared for release. During the reporting period, we hosted two visits from UH personnel, we made two visits to UH to assist in experimental work and discuss results, and we attended a national symposium and the AFOSR program review with funds from this grant. In addition, results of these studies have resulted in the publication of two peer-reviewed articles and the submission of two additional articles to peer-reviewed journals.

Accomplishments

The accomplishments of this program encompass studies of fundamental chemical and tribological phenomena that we seek to extend to practical systems. Therefore, our surface chemical studies have started with small molecules of seemingly little tribological importance to gain a detailed understanding of surface chemical bonding phenomena, and progressed to larger molecules that are more difficult to fully characterize but have a more direct link to lubricants and additives. Similarly, our tribological studies have been conducted on the fundamental level with atomic force microscopy, and we have begun to extend our studies to a more practical level by using a pin-on-disk tribometer housed in an ultrahigh vacuum chamber. Our results will be presented to highlight the meaning of the results on both of these levels.

Small Molecule Interactions—CO and NH₃

Carbon monoxide and ammonia were chosen for study since they have been widely used in the surface science community to investigate surface bonding phenomena. Specifically, CO bonds with a surface through a combination of σ -donor and π -acceptor interactions, while molecular NH₃ adsorbs exclusively as a σ -donor. Any significant difference in the strength of the surface interaction based on the relative abilities of TiC and VC to donate or accept electrons is thus probed. This fundamental behavior will influence the interaction of more complex molecules, lubricants, and additives, with these materials.

We have studied the interaction of CO with TiC and VC (100) using HREELS, complementing the TPD, XPS, and UPS studies done at UH. These experiments have clearly shown that CO adsorbs more strongly to VC than to TiC. Furthermore, the spectroscopic probes have clearly demonstrated that this enhanced bonding is the result of much stronger π -backbonding on the VC (100) surface relative to TiC. Specifically, the TPD results show that CO desorbs from VC at higher temperatures (with first-order kinetics) than it does from TiC, where zero-order kinetics are observed. The HREELS results provide clear evidence for the enhanced backbonding on VC, as the C-O stretching frequency decreases to 2060 cm⁻¹ from the gas-phase value of 2143 cm⁻¹, consistent with donation into the CO 2 π^* level. On TiC, we observe very little CO adsorption under our experimental conditions, and the stretching frequency of reversibly adsorbed CO is 2120 cm⁻¹, demonstrating much less backbonding than is present on VC. The XPS results are consistent with this picture, as demonstrated in the C 1s and O 1s core level CO spectra that have satellite peaks that have greater intensity with weaker surface bonding interactions. The satellites are more intense on the TiC surface, consistent with a weaker bonding interaction. We are working to develop a more quantitative understanding of these surface interactions.

The enhanced tendency for π -backbonding on VC is a direct result of the difference in the electronic structure of the two materials. Since TiC and VC have identical geometric structures, the primary difference in their electronic structures arises from the extra electron present per formula unit of the VC. This electron resides in an orbital that is predominantly V 3d in nature (we believe essentially 3d_{xz, yz}) having a perfect orientation for backbonding with the CO 2 π^* . Alternatively, the highest occupied level in TiC is a C 2p-based level, and no orbitals that are predominantly Ti 3d are occupied, essentially precluding backbonding. Therefore, any surface bonding or reaction that is influenced by the presence of electrons in these orbitals will be different on VC and TiC, and this is borne out in our CO results. Alternatively, the interaction of a σ -donating species should be little influenced by this electronic structure difference, and this is being probed through ammonia adsorption as described below.

Ammonia bonds molecularly to surfaces via the σ -donation of electrons from the 3a₁ molecular orbital into an empty surface orbital. With both VC and TiC, the most reasonable interaction would be with a combination of metal 3d_{z²}, 4s-, and 4p_z-based orbitals, which are all essentially empty on both materials. Therefore, one would expect little difference in the manner in which NH₃ adsorbs on TiC and VC. Thus far, we have only probed this interaction with HREELS studies of NH₃ adsorption at a variety of temperatures. Qualitatively, the two surfaces have very similar interactions with NH₃. Under comparable conditions, the NH₃ loss features have similar intensities on the two surfaces, and appear at similar energies and show comparable shifts with decreasing coverage. Both surfaces lose NH₃ with increasing temperature, retaining similar amounts at 0°C. Our collaborators at UH will be

obtaining TPD and XPS data to quantify the interactions, but the surfaces appear to be coordinating NH_3 in very similar ways, consistent with the σ -donor interaction being comparable on the two surfaces.

Larger Molecules—Alcohols and Trifluoroethanol

To model the interaction of simple hydrocarbon and fluorocarbon lubricants and additives with metal-carbide surfaces, we have studied methanol (MeOH), ethanol (EtOH), and trifluoroethanol (TFE) on both TiC and VC (100) at a variety of temperatures and exposures with HREELS. The OH terminal group on these molecules was chosen to enhance adsorption from the gas in UHV since the sticking probability of the nonpolar alkane is very low, and to provide insight into oxygen-containing basestocks and additives. HREELS shows that these molecules adsorb similarly to both surfaces by forming methoxy, ethoxy, or trifluorethoxy groups at -120°C . These surface states are each characterized by a metal-alkoxy vibration at approximately 350cm^{-1} , demonstrating that the adsorbate bonds to the surface metal atom. The C-O vibration is found at 1050cm^{-1} (MeOH and EtOH) and 1100cm^{-1} (TFE). Different reactivities between the two substrates, and among the various adsorbates, are found when comparing the relative intensities of the spectral features, and different reaction products result from increasing temperature.

In the case of methanol at low temperature (-120°C), we find that the ratio of intensities of the methyl asymmetric C-H stretch to the C-O stretch is greater when adsorbed to VC than to TiC. Since the C-H dipole is oriented perpendicular to the C-O bond, we conclude that the C-O bond is directed more normal to the TiC surface than to the VC surface. As the temperature was increased beyond -65°C , the C-O vibration shifted to 1130 cm^{-1} on VC, but remained at 1050cm^{-1} on TiC. This shift in frequency corresponds to the evolution of reaction products in the TPD spectrum, which shows little reactivity with TiC, but a complex series of products on VC. Additionally, XPS of MeOH on VC showed a shift in the C(1s) feature as the methoxy group changed its chemical configuration. We are working to define the nature of this surface reaction.

With ethanol exposures, the large intensity of the asymmetric C-H vibration in the HREELS spectrum indicates that the C-C bond is oriented more normal to the TiC surface than the VC surface. With increasing temperature on the VC surface, the intensity of C-H vibrational features fell to nearly zero in two steps; the first decrease occurred at -50°C , and the second occurred at 0°C . These temperatures correspond well with the TPD spectra, which show the emission of EtOH at -60°C and 0°C , and the emission of H_2O at 0°C . The C-O bond again shifted to approximately 1130cm^{-1} at 0°C in the HREELS spectrum of EtOH on VC, but no shift was detected on TiC.

The HREEL spectrum of trifluoroethanol on TiC showed a clear C-C vibrational feature at 850 cm^{-1} , while this peak was absent from the spectrum of TFE on VC. Furthermore, as observed with the alcohols above, the relative intensity of the asymmetric C-F stretching vibration was much larger on VC than on TiC. This indicates that the C-C dipole is preferentially oriented closer to the surface normal on TiC than on VC. We were unable to observe the shift in the C-O frequency with increasing temperature since this feature could not be reliably resolved from the C-F stretching vibration. Still, the TPD spectra indicated an array of products from the interaction of TFE with VC.

Tribological Studies—UHV Tribometer

The UHV tribometer used in this work has a ball-on-flat geometry, with orthogonal strain gages mounted on flexures on the arm holding the ball. These orthogonal gages simultaneously measure the applied load and frictional forces measured during motion. The tribometer is housed in an ion-pumped vacuum chamber, and the pressure of the system during operation is 1×10^{-9} Torr. Both the ball and flat are exchangeable under vacuum conditions, such that samples can be cleaned and tested under UHV conditions, and then transferred to our small-spot XPS facility where the wear spot on the ball and the track on the flat can be analyzed. In work applicable to this program, we have used Si_3N_4 balls (Norton NBD 200 material) and TiC-coated 440C balls (CSEM) in a variety of tests under UHV conditions. We've primarily determined the friction coefficient of these materials against 440C and 52100 bearing steels, although we have plans to extend the work to examine TiC-, TiN-, and VC-coated steel flats in our follow-on proposal. This work is intended to emulate the AFM studies described above, but on a macroscopic scale using real engineering materials. The Si_3N_4 ball is the engineering equivalent to the Si_3N_4 AFM tips used in some of our work. The goal is to demonstrate how microscopic properties studied with the AFM influence macroscopic phenomena of technically relevant systems.

Fairly low friction coefficients have been reported for these material combinations in unlubricated sliding in air. For example, the friction coefficient reported for TiC sliding against 440C in air has ranged from 0.1 to 0.2, which is low enough to consider using these materials without lubrication for some applications. However, our results in UHV have produced average dynamic friction coefficients in the range of 0.4 to 0.5 for this combination, levels that are unacceptably high and somewhat erratic. The value of effective lubrication and boundary additives for these systems to lower the friction is quite clear, particularly for vacuum applications as commonly encountered in spacecraft mechanisms.

Relevance to Air Force Mission

Advanced anti-wear materials, such as hard-coated components, are beginning to find use within Air Force, DOD, and NASA spacecraft systems. Specifically, TiC-coated bearing balls are used in the filter wheel mechanisms in the NASA/GOES spacecraft and in the reaction wheels of the NASA/AXAF (Chandra) telescope. These same materials were baselined for the reaction wheels of the SBIRS-Low FDS program. In our experience, even though the hard coatings are improving performance, several questions still remain that require a fundamental understanding of the surface chemistry and tribology of these materials. In general, the same lubricants and additives that have been used with steel components are being used with hard coatings, with little or no insight into chemical incompatibilities or optimization of formulations. For example, the perfluorinated lubricant used in one of these applications appeared to chemically react with and create pits on the TiC-coated ball, making a detailed understanding of the chemical interaction of fluorocarbon species with TiC highly desirable. We seek to provide a fundamental perspective to enable these decisions to be made based on scientific principles.

Our work under this contract represents the first comprehensive study attempting to uncover the detailed surface chemical properties of commercially relevant hard coating materials and to relate this chemistry to tribological performance. To date, our studies have explored how a number of model chemical species (oxygen, water, carbon monoxide, ammonia, and a series of short-chain alcohols) interact with TiC and VC (100) surfaces. These studies lay the groundwork for understanding the reaction of these carbide materials with lubricants and boundary additives used in spacecraft applications. Boundary additives are used to limit friction and wear in mechanical contacts by bonding to, and reacting with, mechanical components. Many of these additives contain oxygen atoms that are surface-active species. Our studies are defining how these additives will react with hard coating materials. Our work has shown that the function of such additives with these materials will likely depend on Lewis base properties of the oxygen sites, their potential for chemical reactions resulting in electron withdrawal from the surface, and specifics of the electronic structure of the carbide surface. We will soon expand our work to study analogs of spacecraft lubricants based upon our understanding of the chemical properties of the materials. In addition, we will conduct surface chemical studies on polycrystalline thin films to correlate engineering materials to our single crystal studies.

Personnel Supported

Dr. Stephen V. Didziulis

Dr. Peter Frantz

Publications

Senguan Lee, Scott S. Perry, Stephen V. Didziulis, Peter Frantz, and Gouri Radhakrishnan, "The Frictional Properties of Titanium Carbide, Titanium Nitride, and Vanadium Carbide: Measurement of a Compositional Dependence with Atomic Force Microscopy," *J. Vac. Sci. Tech.*, in press

Stephen V. Didziulis, Peter Frantz, Scott S. Perry, Oussama El-bjeirami, Syed Imaduddin, and Philip Merrill, "Substrate Dependent Reactivity of Water on Metal Carbide Surfaces," *J. Phys. Chem.*, in press.

Philip B. Merrill, Scott S. Perry, Peter Frantz, Stephen V. Didziulis, "Adsorption of Water on TiC(100): Evidence for Complex Reaction and Desorption Pathways," *J. Phys. Chem.*, 102 (39), 7606–7612 (1998).

Peter Frantz and Stephen V. Didziulis, "Detailed Spectroscopic Studies of Oxygen on Transition Metal Carbide (100) Surfaces," *Surface Science*, 412-413 (1-3), 384-396 (1998).

Interactions/Transitions

Presentations: Dr. Didziulis spoke at the National Meeting of the American Chemical Society in Anaheim, March 24, 1999. The title of the presentation was "Fundamental Chemical and Tribological Studies of Transition Metal Carbides."

Consultative and Advisory Functions: Dr. Didziulis consults on a regular basis with personnel from the Lubricant Group of the Non-Structural Materials Branch at AFRL (Wright Laboratory). These personnel include C. E. Snyder, L. Gschwender, and J. Zabinski. Topics discussed in these meetings are the development of new spacecraft lubricants and the use of hard coatings on ball bearing surfaces. These interactions have occurred at Aerospace and at WL. In addition, the primary function of The Aerospace Corporation is to advise USAF/SMC and classified customers on matters related to the design and manufacture of spacecraft systems. We participate in numerous technology development programs that will directly benefit from the knowledge gained in this work. We provide a direct path for the insights gained in this research for implementation in current and future AF and DOD space systems.

Transitions: While we have made no direct transition of information from this program, we strongly believe that we will make a significant contribution to the use of hard coatings in spacecraft systems. We interact with satellite component manufacturers (e.g., Honeywell) that have numerous AF and DOD programs investigating the use of hard-coated ball bearing components, and we work with NASA on reaction wheel systems that include hard-coated ball bearing components. This work will provide insight into the lubrication of these hard-coated components when it is coupled to our ongoing work in support of these numerous programs.

New Discoveries, Inventions, Patent Disclosures

The scientific discoveries based upon the research performed under this contract have been described in the accomplishments section as well as submitted for publication in peer-reviewed journals.

Honors/Awards

None